10.6 LABORATORY CCN MEASUREMENTS OF ORGANIC SUBSTANCES

James G. Hudson
Desert Research Institute,
Reno, Nevada

1. INTRODUCTION

There are several reasons that the indirect aerosol effect is the largest climate uncertainty. The basis of the uncertainty is the dual complexity of the preexisting aerosol that causes the indirect effect and the clouds that manifest the indirect aerosol effect. Cloud condensation nuclei (CCN) measurements offer an important simplification of the problem be allowing these complexities to be separated. In theory CCN spectra provide all the information that is needed about the aerosol to predict and determine the effects of the aerosol on clouds; i.e., changes in cloud albedo and precipitation efficiency, which also alters cloudiness, which in turn alters planetary albedo. CCN measurements then allow the aerosol effects to be decoupled from complex cloud dynamic processes.

Until a few years ago it was thought that nearly all CCN were inorganic salts such as ammonium sulfate and sodium chloride, which are known to obey Kohler (1926) theory (Gerber et al. 1977). However, there has been increasing evidence of organic atmospheric aerosol (e.g., Saxena and Hildemann 1986) and even organic CCN (Novakov and Penner 1996). Organic material has generally been neglected as CCN because of : 1) higher molecular weights; 2) lower densities [both of which tend to make fewer ions per unit mass] and 3) a smaller percentage of ions that dissolve in water (i.e., lower van't Hoff factors). Most inorganic salts are highly soluble; i.e., nearly all ions go into solution (e.g., the van't Hoff factor for NaCl is 2). Nevertheless, some organics do make CCN (Cruz and Pandis 1997). Moreover and on the other hand, organic material may have other water nucleating properties that are different from inorganics. These properties include: 1) alterations of surface tension (Li et al. 1998; Facchini et al. 1999); 2) partially solubility (Shulman et al. 1996; 1997; Kulmala et al. 1997; Laaksonen et al. 1998) (i.e., greater dissolution with more dilution); and hydrophobic coatings (Bigg 1986;Garrett 1971; Kocmond et al. 1972; Podzimek and Saad 1975; Otani and Wang 1984). All three of these effects could alter Kohler theory, which maintains that each CCN has a similarly shaped curve that relates the equilibrium size of the solution droplet to the ambient humidity. The Kohler curves can be uniquely characterized by a peak or critical supersaturation (S_c). Particles with the same S_c, which is related to the number of soluble ions, should then have the same nucleating and growth characteristics. If organic material alters the shapes of Kohler curves then S_c would not uniquely characterize nucleation and growth of droplets on those particles. This would not only impact the measurement of CCN but also the application of CCN measurements to the atmosphere. Kohler theory is the basis of the assumption that CCN behave the same in the artificial controlled environments of cloud chambers and in real clouds; that is apart from dynamic factors that would expose various particles to different supersaturations. Another way of putting this is that the hierarchy of nucleation growth potential represented by S_c should hold under all humidity conditions. In other words particles that have lower S_c values should always make larger droplets than higher S_c particles. If this is not the case then CCN measurements and the application of CCN spectra to the atmosphere (e.g., to predict cloud droplet concentrations) is considerably compromised.

Hudson and Da (1996) showed the tendency of CCN in polluted air masses to have relatively larger dry particle sizes than CCN in cleaner air masses. The larger sizes could be due to greater insoluble components that are internally mixed with inorganic CCN or to less soluble material such as organics, which would require greater mass to produce the same S_c. An important question is whether organic material actually participates in nucleation by actually contributing soluble ions as opposed to being a passive component.

James G. Hudson
Desert Research Institute
Reno, NV 89512-1095
Email: hudson@dri.edu

2. EXPERIMENT

In order to determine the nucleation properties of organic material laboratory measurements were made of S_c as a function of the dry particle sizes of some organic substances. Aerosols were prepared in solution, atomized and passed through an electrostatic classifier (EC or DMA-differential mobility analyzer) set at various voltages. Since these measurements were made with the two Desert Research Institute (DRI) CCN spectrometers (Hudson 1989) this also provided limited tests of Kohler theory. Size-S_c measurements with these two chambers were also made of some ambient aerosols.

The DRI CCN spectrometers (Hudson 1989) depend even more on Kohler theory than other CCN instruments because they use the sizes of the droplets that are produced in the cloud chambers to deduce S_c of the particles. It is assumed that lower S_c particles always produce larger droplets. The violations of Kohler theory outlined above could produce situations where some particles could pass others in terms of relative sizes as the droplets grow in the same supersaturation fields. I.e., the effect (reduction) on surface tension should diminish as droplets grow and thus dilute. Therefore, a droplet grown on a particle that reduces surface tension, which makes it a better nucleus, could produce a larger droplet than a similar particle that does not reduce surface tension. Since the reduction of surface tension diminishes with increased dilution this could allow the other droplet to catch up or even pass the surface-tension-reduced droplet. Likewise a particle that is partially soluble may become a better nucleus as the droplet dilutes with growth. It could then possibly pass or catch up with another drop that has the same amount of dissolved material throughout its lifetime. Likewise a drop with a hydrophobic coating that inhibits condensation may catch up or pass another drop after the monolayer becomes too small and bursts. These possibilities can be tested by using the two DRI CCN spectrometers at different droplet size ranges. Different droplet size ranges are achieved by using different supersaturations and or airflow rates in the two cloud chambers. Since the calibrations are done with standard inorganics such as sodium chloride the procedure amounts to a comparison between the growth of NaCl and the test aerosol. The S_c of the size classified NaCl is known (Gerber et al. 1977) so that the S_c of the test aerosol can be deduced from the size of the droplets it produces relative to the calibration aerosol. Violations of Kohler theory could show different droplet sizes relative to the calibration aerosol, that is different deductions of S_c in the two instruments. But if the particles produce the same relative droplet sizes (same S_c) in both chambers then this would indicate that significant violations of Kohler theory have not occurred. This experiment is best done with monodisperse aerosol.

3. RESULTS

Table 1 summarizes measurements of 3 inorganics and 9 organic aerosols. The hygroscopicity parameter, B, is the coefficient of the Raoult or nucleus term of the Kohler equation. B is proportional to density and van't Hoff factor, i, and inversely proportional to molecular weight. It is notable that oxalic acid is just as soluble as the inorganics. But most inorganics were as expected not nearly as good as nuclei as the inorganics. B and i were calculated at two extreme particle sizes because unlike most inorganics some of the organics showed nucleating properties that were size dependent. For instance glutaric acid was a better nucleus at larger sizes as shown in Fig.1, where the data points are closer to the inorganic line at larger sizes than at smaller sizes. Sodium dodecyl (lauryl) sulfate (SDS) on the other hand shows opposite behavior (Fig. 2). Figs. 3 and 4 show that mixtures of SDS and NaCl do not show nonlinear behavior.

Fig. 5 shows that both CCN spectrometers found the same CCN concentrations for ambient size classified aerosol. The distributions were much wider than the calibration aerosol because of variations in composition in the ambient. Nevertheless all particles seem to have been measured by both CCN spectrometers in these cases. Fig. 6 shows that both spectrometers deduced similar median S_c values. This does not suggest violations of Kohler theory. Figure 7 shows that both instruments deduce that the ambient particles are significantly larger than sodium chloride or ammonium sulfate particles. This suggests that they are either composed of internal mixtures of soluble and insoluble material and/or they are composed of less soluble material such as organics. Indeed they show similar size-S_c relationships to some of the pure ogranic aerosols that were tested in the laboratory. This was a continental air mass with moderate pollution.

Figs. 1-7 showing agreement between the two spectrometers suggests no significant violations of Kohler theory.

Substance	Molucular mass, M	density	hygroscopicity parameter B			effective van’t Hoff factor, i	
			“theory” *	measured @ 20 nm	measured @ 200 nm	@ 20 nm	@ 200 nm
NaCl	58.4	2.165	1.30	---	---	2	2
$(NH_4)_2SO_4$	132.14	1.769	0.64	0.52	0.53	2.44	2.49
KI	166	3.13	0.60	0.57	0.59	1.87	1.95
Oxalic acid	90.04	1.90	0.68	0.57	0.63	1.65	1.96
Benzoic acid	122.12	1.27	0.33	0.47	0.45	2.8	2.7
Glutaric acid	132.11	1.42	0.34	0.044	0.18	0.17	1.02
Adipic acid	146.14	1.36	0.30	0.022	0.044	0.15	0.29
Pinonic acid	184.24	1.23	0.21	0.04	0.004	0.35	0.03
Stearic acid	284.49	0.94	0.11	0.03	0.007	0.55	0.13
SDS	288.38	0.40	0.05	0.35	0.077	6.66	1.44
Urea	60	1.33	0.68	0.003	0.008	0.01	0.19

Table 1. Size versus supersaturation relationships for 3 inorganics and 9 organic aerosols
* assuming full dissociation, i = 2 for NaCl, KI, and organics, i = 3 for ammonium sulfate

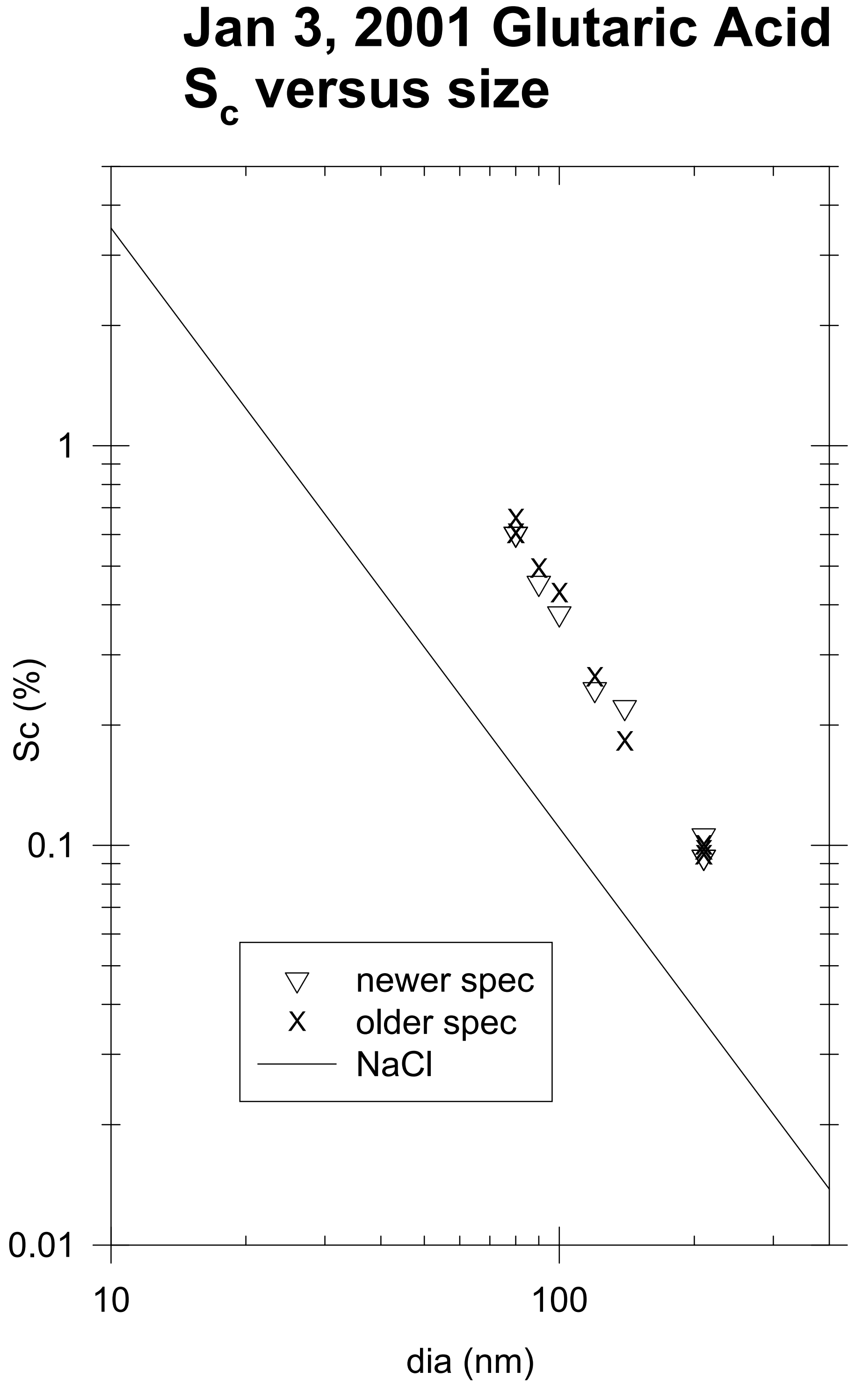


Fig. 1. Size versus S_c relationship for glutaric acid. Also shown is the theoretical relationship for NaCl.

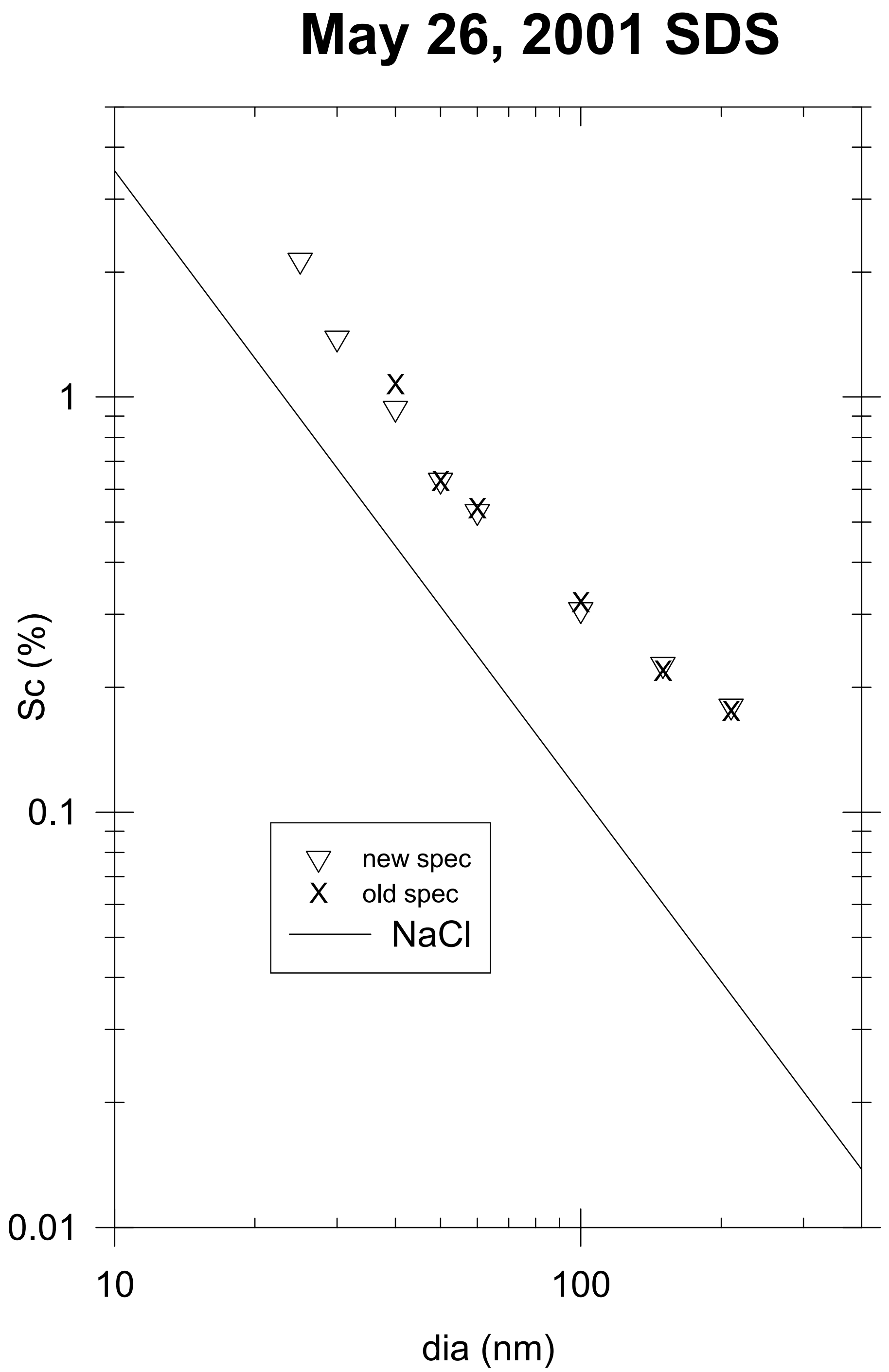


Fig. 2. Size versus S_c relationship for sodium dodecyl sulfate.

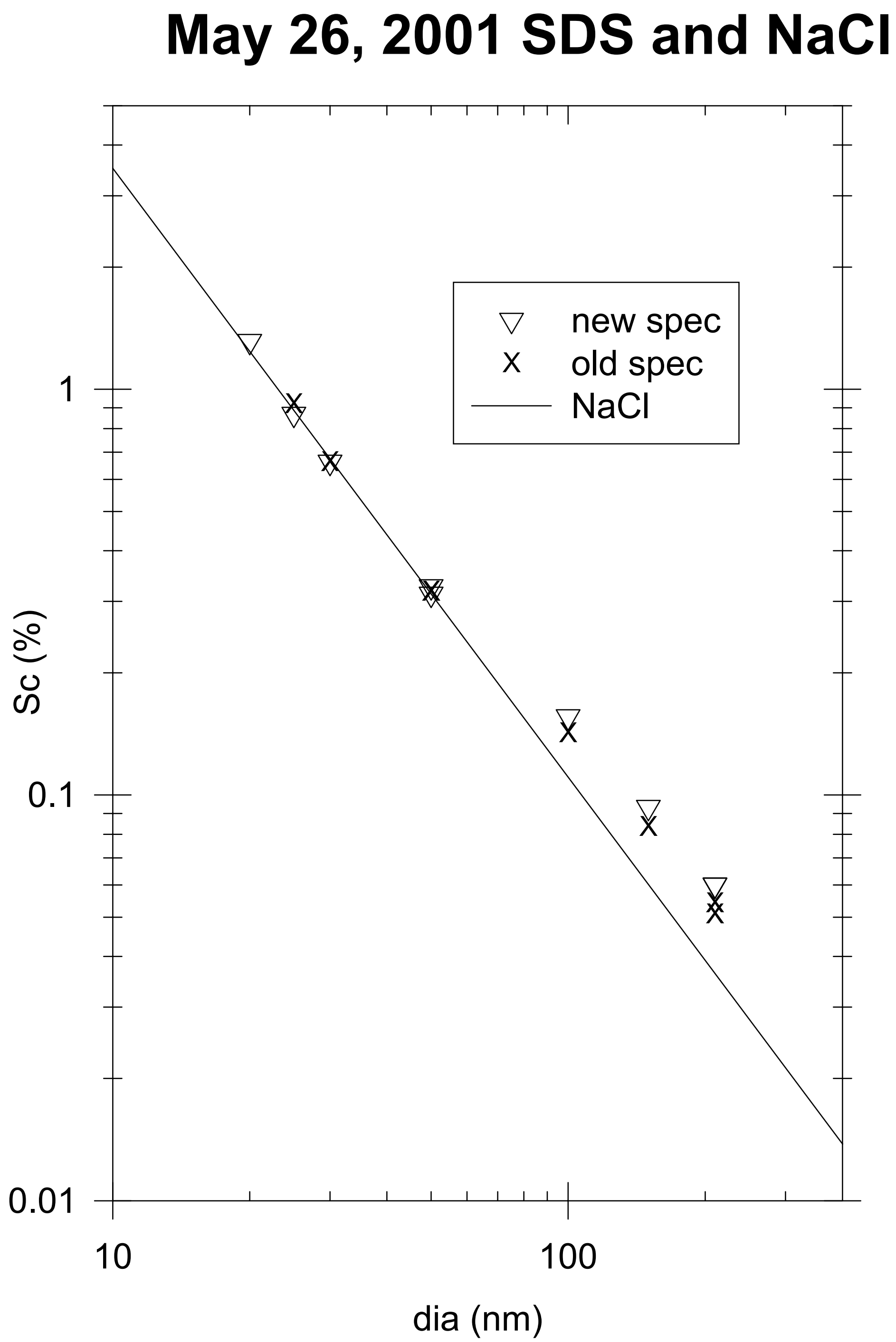


Fig. 3. Size versus S_c relationship for an internal mixture of sodium chloride and sodium dodecyl sulfate.

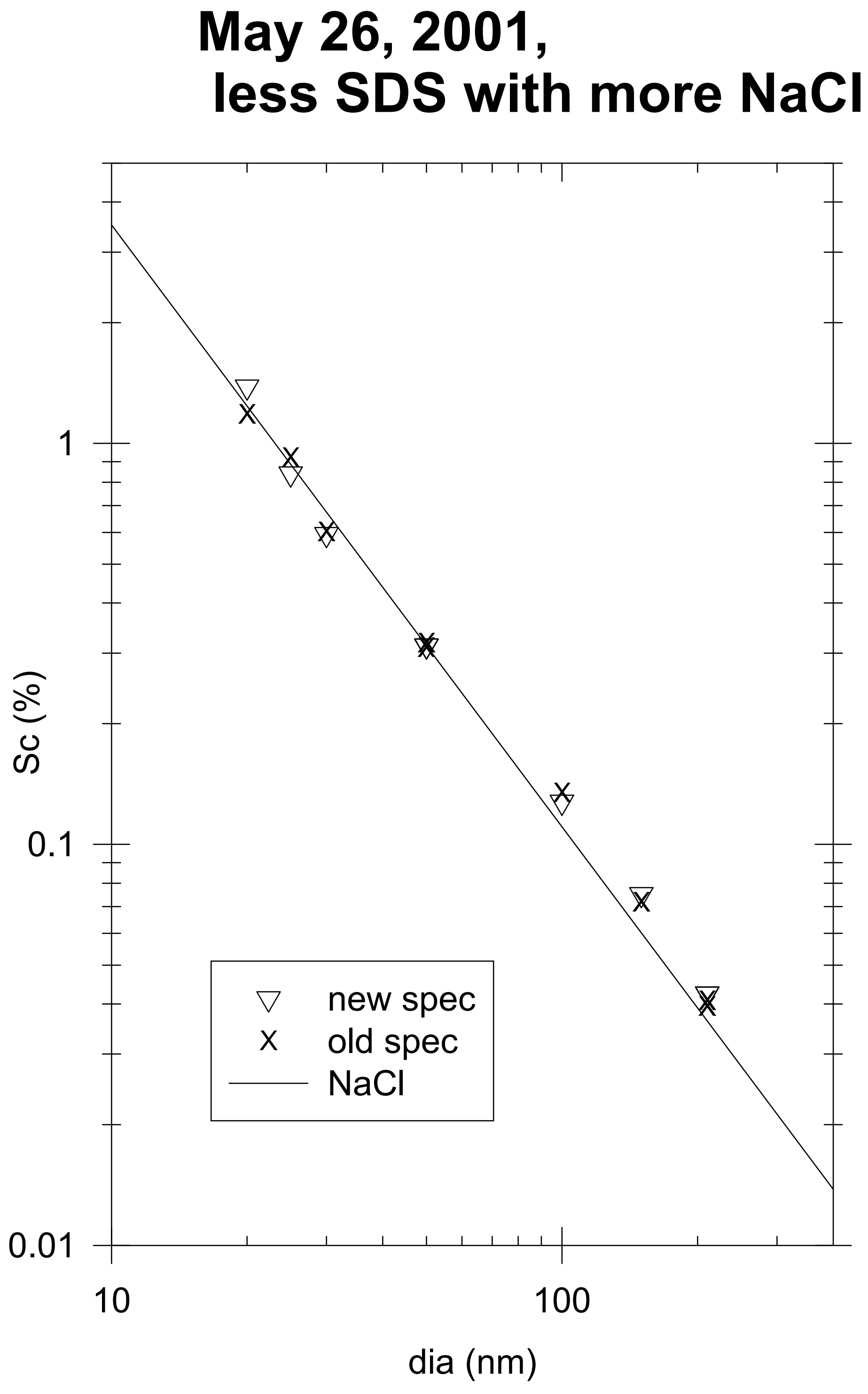


Fig. 4. As Fig. 3 but with a greater proportion of NaCl to SDS.

Fig. 5. Ratio of concentrations in the two CCN spectrometers.

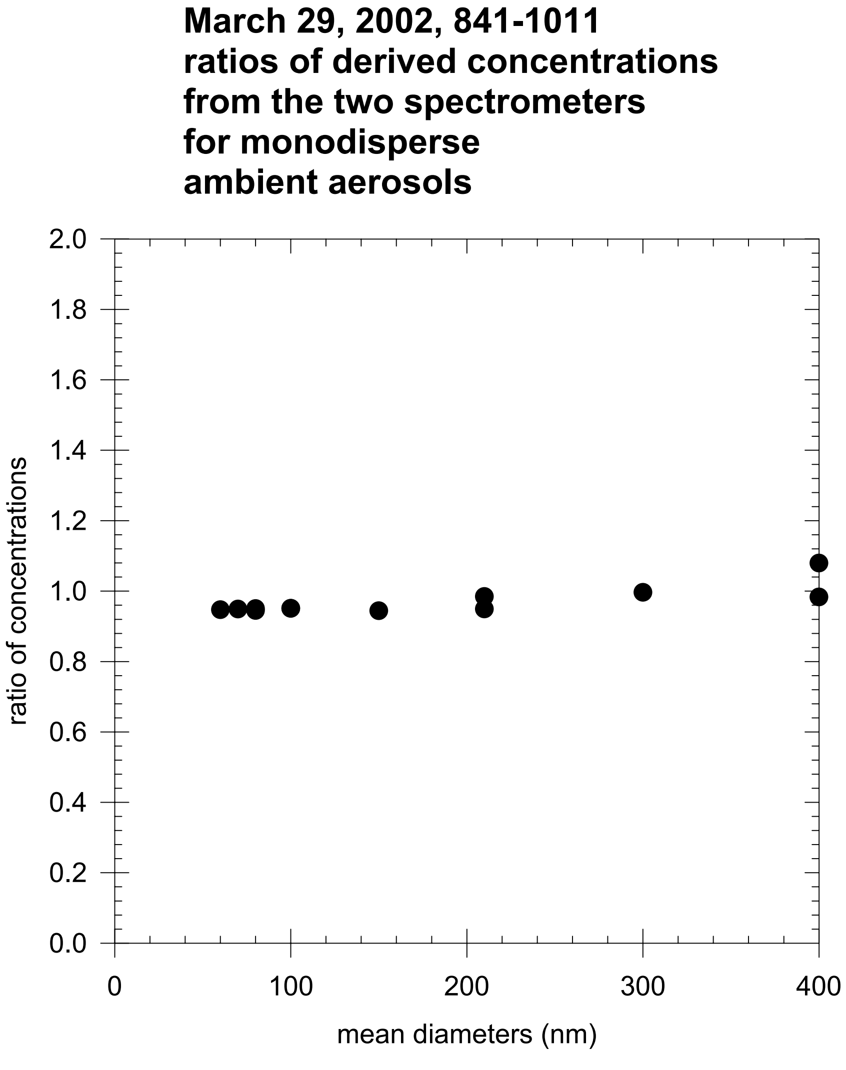
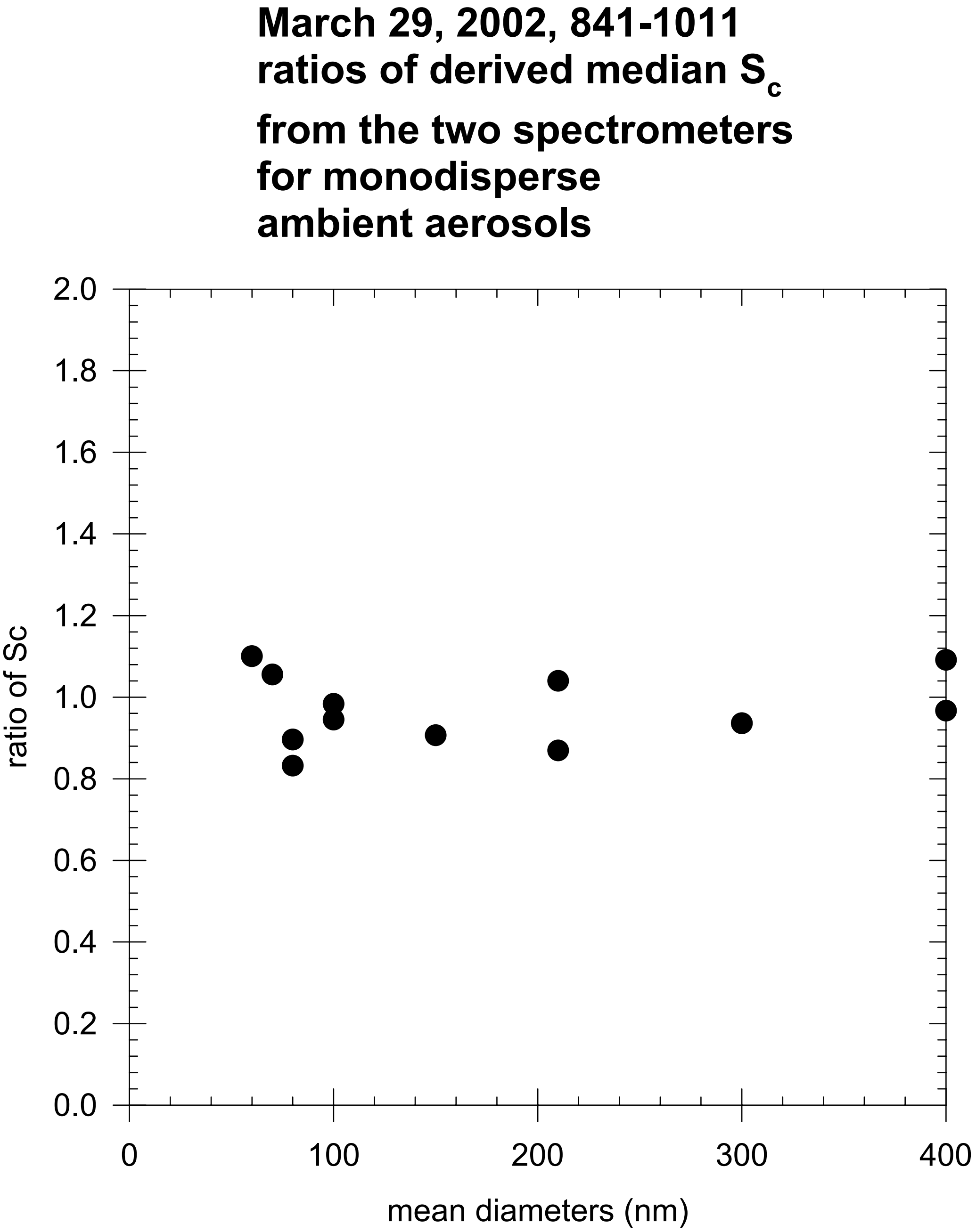


Fig. 6. Ratio of S_c from the two chambers for ambient aerosol.



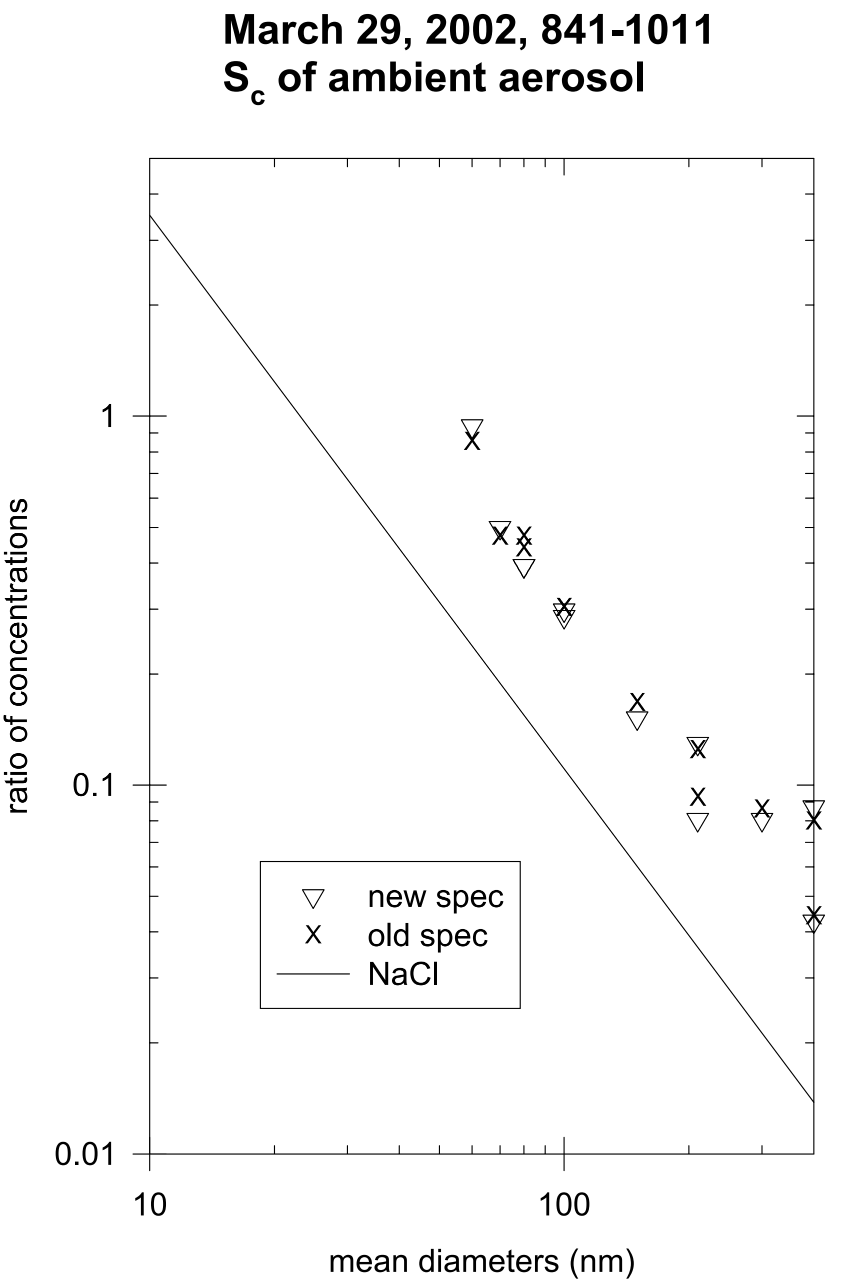


Fig. 7. Size versus S_c relationships for ambient aerosol.

4. References

Bigg, E.K., J.L. Brownscombe, and W.J. Thompson, 1969: Fog modifiction with long-chain alcohols. *J. Appl. Meteor.*, **8,** 75-82.

Cruz, C.N., and S.N. Pandis, 1997: A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei. *Atmos. Environ.* **31**, 2205-2214.

Facchini, M.C., M. Mircea, S. Fuzzi, and R.J. Charlson, 1999: Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature,* **401,** 257-259.

Garrett, W.D., 1971: Retardation of water drop evaporation with monomelecular surface films. *J. Atmos. Sci.*, **28**, 816-819.

Gerber, H.E., W.A. Hoppel, and T.A. Wojciechowski, 1977: Experimental verifications of the theoretical relationship between size and critical supersaturation of salt nuclei. *J. Atmos. Sci.,* **34**, 1836-1841.

Hudson, J.G., 1989: An instantaneous CCN spectrometer. *J. Atmos. & Ocean. Tech.*, **6**, 1055-1065.

Hudson, J.G. and X. Da, 1996: Volatility and size of cloud condensation nuclei. *J. Geophys. Res.,* **101**, 4435-4442.

Kocmond, W.C., C.F. Rogers, U. Katz, J.G. Hudson and J.E. Jiusto, 1982: The 1980 International Cloud Condensation Nuclei Workshop. *Idojaras*, **86**, No. 2_4, 160_168.

Laaksonen, A., P. Korhonen, M. Kulmala, and R.J. Charlson, 1998: Modification of the Kohler equation to include soluble trace gases and slightly soluble substances. *J. Atmos. Sci.*, **55**, 853-862.

Li, Z., A. Williams, and M. Rood, 1997: Influence of surface active organics on the activation of aerosol particles containing organic and inorganic solute, *J. Atmos. Science*, **25**, 1859_1866.

Kulmala, M.A., P. Laaksonen, R.J. Charlson, and P. Korhonen, 1997: Clouds without supersaturation. *Nature*, **388**, 336-337.

Novakov, T., and J.E. Penner, 1993: Large contribution of organic aerosols to cloud condensation nuclei concentrations. *Nature,* **365**, 323-365.

Otani, Y., and C.S. Wang, 1984: Growth and deposition of saline droplets covered with a monolayer of surfactant. *Aerosol Sci. Technol.*, **3,** 155-166.

Saxena, P. and Hildemann, L.M. (1996) Water_soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds. *J. Atmos. Chem.*, **24**, 57_109.

Shulman, M.L., R.J. Charlson, E.J. Davis, 1997: The effects of atmospheric organics on aqueous droplet evaporation. *J. Aerosol Sci.*, **28,** 753-788.

Shulman, M.L., M.C. Jacobson, R.J. Charlson, R.E. Synovec, and T.E. Young, 1996: Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets. *Geophys. Res. Let.* **23**, 277-280.